FUNDAMENTAL PRINCIPLES OF WATER CONDITIONING

1. GENERAL

1.01 This section outlines the fundamental principles of water
      conditioning. The effect of impurities on the characteristics of water
      are discussed together with brief descriptions of water softening
      treatments and methods of corrosion prevention.

1.02 This section replaces Section 770-230-300. Whenever this section is
      reissued, the reason for reissue will be listed in this paragraph.

2.   BASIC CHEMICAL PRINCIPLES INVOLVED IN WATER CONDITIONING

2.01 To facilitate understanding of the fundamental principles used in
      water conditioning, this paragraph reviews briefly the chemistry
      involved.

2.02 The basic substances of which all others are composed are called
      elements. Those most commonly encountered in water conditioning,
      together with their chemical symbols, are given in the following
      table:

NAME	SYMBOL	NAME	SYMBOL
Calcium	Ca	Oxygen	O
Carbon	C	Phospherous	P
Chlorine	Cl	Potassium	K
Hydrogen	H	Silicon	Si
Iron	Fe	Sodium	Na
Magnesium	Mg	Sulfur	S

These elements have definite unit weights and always combine in
definite proportions when they unite to form chemical compounds. A
familiar example is water in which hydrogen is combined with oxygen in
the ratio of two parts of hydrogen to one part of oxygen and is
expressed by the formula H_2O. Compounds frequently contain more than
two elements, for example, sodium carbonate which is written Na_2CO_3 and
consists of two parts of sodium (Na) combined with one part of carbon
and three parts of oxygen.

2.03 A number of the compounds encountered in water analysis as well as
      their chemical formula and relative solubility in water are given in

the table on Page 3. Some of these compounds are more commonly available with water of crystallization such as $Na_3PO_4.12H_2O$ and $Na_2SiO_3.5H_2O$. With the exception of iron oxide (ordinary rust), which is red in color, all of these compounds are white powders.
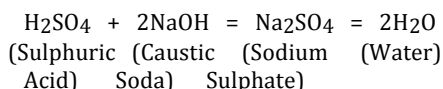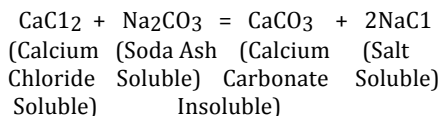
2.04 When chemical compounds are dissolved in water, they disassociate (split up) into two parts each of which carries an electrical charge. These parts are called ions, one of which is positively charged and the other negatively charged. Hydrogen and the metals (calcium, iron, magnesium, sodium, etc) carry positive charges while the remaining elements of the compound are negatively charged. Compounds are formed by the union of positive and negative ions. Since like charges repel each other, positive ions will not react with positive ions or negative ions with negative ions.

2.05 Chemical compounds may be broadly classified as acids, alkalies (also called bases) and salts. Acids are comprised of hydrogen ions and so-called acid radicals. For example, sulphuric acid has the formula H_2SO_4, the SO_4 group being the acid radical. Alkalies are comprised of a metallic element and a hydroxyl group. For example, lye (sodium hydroxide) has the formula NaOH. The OH portion is the hydroxyl group. Salts are the result of chemical reactions between acids and alkalies.

2.06 When a water solution of an acid is mixed with a water solution of an alkali, they will react to form a normal salt and water as shown by the following reaction:

$$H_2SO_4 \ + \ 2NaOH \ = \ Na_2SO_4 \ = \ 2H_2O$$
(Sulphuric (Caustic (Sodium   (Water)
   Acid)   Soda)   Sulphate)

It will be noted that the equation balances, i.e., on each side of the equal sign will be found the same elements (H, S, Na, O) in the same proportions although differently arranged. If two soluble salts are combined where one of the possible reaction products is insoluble, the reaction will always proceed to form the insoluble compound. The following is a typical example:

$$CaCl_2 \ + \ Na_2CO_3 \ = \ CaCO_3 \ + \ 2NaC1$$
(Calcium (Soda Ash (Calcium   (Salt
 Chloride Soluble) Carbonate   Soluble)
 Soluble)   Insoluble)

It will be noted that the equation balances since there are on each side of the equal sign one Ca, two C1, two Na, one C, and three O.

If two soluble neutral salts are mixed where the possible reaction products are also soluble, no reaction will take place. For example,

if solutions of sodium chloride and magnesium sulphate are mixed, no reaction will result since sodium sulphate and magnesium chloride are both soluble salts.
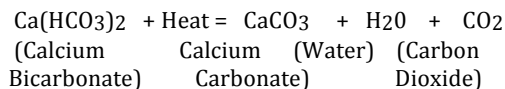
Salts may show a neutral, basic or acid reaction to indicators such as litmus paper, methyl orange, or phenolphthalein. For example, sodium carbonate is alkaline, sodium acid sulphate is acid, and sodium chloride is neutral in reaction to these indicators.

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COMPOUNDS	FORMULA	SOLUBILITY IN WATER
Calcium Chloride	$CaCl_2$	Very soluble
Calcium Sulphate	$CaSO_4$	Slightly soluble
Calcium Bicarbonate	$Ca(HCO_3)_2$	Soluble
Calcium Carbonate	$CaCO_3$	Slightly soluble
Calcium Hydroxide	$Ca(OH)_2$	Fairly soluble
Iron Oxide	Fe_2O_3	Insoluble
Magnesium Chloride	$MgCl_2$	Very Soluble
Magnesium Sulphate	$MgSO_4$	Soluble
Magnesium Bicarbonate	$Ng(HCO_3)_2$	Soluble
Magnesium Carbonate	$MgCO_3$	Slightly soluble
Magnesium Hydroxide	$Mg(OH)_2$	Insoluble
Sodium Chloride	$NaCl$	Very Soluble
Sodium Carbonate	Na_2CO_3	Very Soluble
Sodium Silicate	$1Na_2O:3.2SiO_2$	Difficultly soluble
Sodium Metasilicate	$1Na_2O:1SiO_2$	Very Soluble
Sodium Hydroxide	$NaOH$	Very Soluble
Trisodium Phosphate	Na_3PO_4	Very Soluble
Tetrasodium Pyrophosphate	$Na_4P_2O_7$	Very Soluble
Sodium Hexa Metaphosphate	$(NaPO_3)_6$	Very Soluble
Disodium Phosphate	Na_2HPO_4	Very Soluble

2.07 Reactions are generally accelerated by increased temperatures. In the case of relatively unstable compounds, heat alone is sufficient to produce a chemical reaction. For example, the bicarbonates decompose on heating to form carbonate, water and carbon dioxide gas as shown by the following equation:

$$Ca(HCO_3)_2 \ + Heat = \ CaCO_3 \ \ + \ H_2O \ \ + \ \ CO_2$$
   (Calcium   Calcium   (Water) (Carbon
   Bicarbonate)   Carbonate)   Dioxide)

The above is the typical reaction that takes place when scale forms in boilers and air conditioning systems.

3. CHARACTERISTICS OF WATER

3.01 All natural waters contain impurities, the quantities present varying widely. These may include suspended matter, mineral salts, gases

absorbed from the atmosphere, contamination from industrial wastes and bacteria. Public water supplies are usually subject to treatment such as sedimentation, filtration and chlorination to insure a clean, potable water free from bacteria. Although softening of public

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supplies is practiced to some extent, as water is received from the mains it generally still contains most of the dissolved mineral salts and gases which are the chief causes of scale formation and corrosion.

3.02 Classification by Hardness: Water is classified as soft or hard depending upon the amount of dissolved mineral salts, principally calcium and magnesium bicarbonates, sulphates and chlorides. While there is no sharp demarcation between soft and hard waters, the U.S. Geological Survey has classified all waters into four groups depending upon the total mineral salts content expressed in terms of parts per million of calcium carbonate ($CaCO_3$). This classification is given below:

Class 1 (soft) 1 to 60 parts per million
Class 2 (slightly hard) 61 to 120 parts per million
Class 3 (hard) 121 to 180 parts per million
Class 4 (very hard) more than 180 parts per million

While for ordinary use the hardness in Class 1 is scarely noticeable, as the upper limit is approached softening is frequently practiced for steam boiler plants and a few industrial uses. In the case of Class 2 waters, some softening is indicated usually consisting of internal softening within a boiler. For Class 3 and Class 4 water, softening is obligatory to avoid excessive heat losses in boiler operation. Softening of public supplies is generally practiced only in the case of Class 3 and Class 4 water and usually only to the extent of reducing the hardness to the Class 2 level.

Temporary and Permanent Hardness: There are two types of hardness; temporary or carbonate hardness and permanent or non-carbonate hardness. When hard water is boiled, the calcium and magnesium bicarbonates decompose liberating carbon dioxide gas and forming calcium and magnesium carbonates. The carbonates being less soluble than the bicarbonates, and even more insoluble in hot than cold water, most of the calcium and magnesium carbonates are precipitated out. The amount by which the hardness of water is thus decreased by boiling is the temporary hardness. The residual hardness due to the calcium and magnesium sulphates and chlorides is unaffected by boiling and is the permanent hardness.

3.03 Corrosion Factors - The pH Scale: Water is classified as corrosive or non-corrosive depending upon whether it is acid or alkaline and to a degree upon the kind and quantity of mineral salts and dissolved gases which it contains. The degree of acidity or alkalinity of a particular sample of water may be determined by an electrical meter calibrated in a special scale called the pH scale. The pH of a liquid may also be determined approximately by the use of certain dyes which change color at different degrees of acidity or alkalinity. The pH scale runs from 0 for the strongest acid to approximately 14 for the strongest alkali. The mid-point of 7.0 represents neutrality. The scale is logarithmic

so that a pH of 6.0 is ten times as acid as a pH of 7.0, a pH of 5.0 is
100 times as acid as a pH of 7.0, etc. Oxygen and carbon dioxide in
water although generally present only to the extent of a few parts per
million are the chief causes of corrosion. Oxygen is the actual
corrosive

agent, but the presence of carbon dioxide renders the water acidic and
accelerates the reaction. Due to solubility factors, these gases are
more soluble in cold than in hot water. Accordingly some waters may be
more corrosive in winter than in summer. The pH value and gaseous
content alone are not a complete measure of the relative corrosiveness
of different waters, however, since many hard waters form a protective
carbonate scale and accordingly are less corrosive than soft waters.

4.   WATER SOFTENING PROCESSES

4.01 There are five principal ways that water may be softened: (1) by
distillation, (2) by base-exchange zeolites, (3) by precipitation with
chemicals, (4) by acid treatments, and (5) by the sequestering action.
These are discussed below.

Distillation: If water is evaporated to steam, the non-volatile
impurities, including the mineral salts, remain behind in the
evaporator and the condensate consists of soft water. While having
only limited industrial application, this method is used by the larger
power stations where only a relatively small amount of make-up water is
required.

Base-Exchange Zeolites: In the zeolite process, the hard water is
passed through a bed of insoluble material, known as zeolite, which has
the remarkable property of exchanging its sodium content for the
calcium and magnesium of the hard water. While there are several types
of zeolite, both natural minerals and synthetic compounds, the most
commonly used types are essentially sodium aluminum silicates. By this
exchange the water is softened since the scale forming hard water salts
present in the raw water have been replaced by corresponding sodium
salts which are not scale forming. Eventually the zeolite becomes
exhausted and must be regenerated. This is accomplished by passing a
solution of sodium chloride (common salt) through the bed which re-
verses the process, driving out the calcium and magnesium that have
been taken up from the raw water and replacing them with a fresh supply
of sodium. The intervals between regenerations depend upon the hard-
ness of the water being treated and the capacity of the zeolite
softener. Since the regeneration step may take several hours or
longer, it is considered good practice to have two beds to insure a
steady supply of softened water. Zeolite softened water approaches
zero hardness but shows no substantial change in pH and no reduction of
total solids. This treatment is frequently used in hard water
districts to condition all of the water used in a building.

Synthetic resin exchange materials have been developed that not only
soften water by the removal of the calcium and magnesium but actually
completely remove all the mineral salts present. This process known as
"demineralization" operates in two stages and produces a treated water
approaching distilled water in purity.

Chemical Precipitation: As pointed out in a previous section, the hardness of water is largely due to the presence of soluble calcium and magnesium salts, principally bicarbonates, sulphates and chlorides. By the addition of suitable chemicals, these can be converted into insoluble compounds and precipitated. The water is thus rendered soft. Chemicals commonly used for this purpose include soda ash (sodium carbonate), trisodium phosphate, and water

glass (sodium silicate). These compounds react with the calcium and magnesium salts in the water to form calcium and magnesium carbonates, phosphates or silicates which are insoluble and precipitate as sludge. The treatment may be external, i.e., on the water supply, or internal, as within a boiler.

In the case of internal treatment, the chemicals are introduced directly into the boiler. The purpose of the treatment is to precipitate the calcium and magnesium salts in the form of a loose sludge that may be removed in the blowdown.

The Lime-Soda Process: A typical external treatment is the lime-soda process. This consists of adding to the water a mixture of hydrated lime (calcium hydroxide) and soda ash (sodium carbonate) in an amount determined by the analysis of the raw water. The lime reacts with the temporary bicarbonate hardness to form calcium and magnesium carbonates. The calcium carbonate is insoluble and settles out. The magnesium carbonate is partially soluble and reacts with additional lime to form magnesium hydroxide which is insoluble and precipitates. The soda ash reacts with the permanent, non-carbonate hardness (calcium and magnesium sulphates and chlorides) to form calcium and magnesium carbonates and the above process is repeated. The treatment may be made cold but heat accelerates the reactions. The sludge formed is allowed to settle and the softened water is filtered or drawn off. This treatment has its principal application where large volumes of water are conditioned such as for public supplies and industrial uses.

Acid Treatment: In certain highly alkaline natural waters where the pH runs over 8.3, the only economical procedure is to acid treat cooling tower water. This prevents the formation of calcium carbonate scale, increases possible cycles of concentration and prevents delignification of tower wood. Feeding devices operating on pH controls are required. While sulphuric acid is commonly used, sodium bisulphate and sulphamic acid are suitable solid materials that avoid any handling hazards.

Sequestering Action: Certain phosphates have the property when mixed with hard water of so combining with hard water salts as to render the water soft without actually precipitating the calcium and magnesium present. This property has been termed sequestering action. While tetrasodium pyrophosphate and certain polyphosphates possess this characteristic, it is most marked in the metaphosphates. These phosphates have accordingly been widely used for the prevention of hard water deposits in water lines and air conditioning systems. It has been found that even when present in minute quantities, as little as 1 or 2 parts per million, this chemical has the ability of preventing the precipitation of hard water compounds, particularly calcium carbonate. This treatment is particularly adapted

for the prevention of hard water deposits in water lines and air
conditioning systems. It is not effective for boiler water treatment as
these phosphates decompose and lose their sequestering properties at
boiler water temperatures.

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Organic sequestering agents, also called chelating agents, are more
powerful and more stable than the polyphosphates. The most common are the
salts of ethylenediamine tetra acetic acid, for convenience known as EDTA.
While highly effective, the use of these materials in water conditioning
has been limited by their relatively high cost.

5. CORROSION - GENERAL

5.01 Chemical Corrosion: Water combines with iron or steel to produce
ferrous hydroxide. This compound is alkaline in reaction and tends to
slow down the process of corrosion. However, if the water contains
dissolved oxygen or is acidic in nature, the film is destroyed and
corrosion continues with the formation of rust (iron oxide). Iron oxide
is porous and water tends to penetrate it to reach the metal. Except
for the effect of protective films as discussed in Paragraph 3.03, the
amount of corrosion to be expected is almost directly related to the
quantity of dissolved oxygen present and the degree of acidity (pH) of
the water. Further factors tending to accelerate corrosion are
increases in temperature and the velocity of motion of water over the
metal surface. The presence of salts such as chlorides and sulphates
also has a contributing effect.

5.02 Electrochemical Corrosion: Another form of corrosion of iron or steel
which results in pitting of the metal is attributed to electrochemical
action. If dissimilar metals are placed in contact in water, an
electric cell is formed. The current flows from the more corrodible
metal (the anode) to the less corrodible metal (the cathode) carrying
into solution the more corrodible metal. The direction of the current
flow depends upon the position of the metals in the electrochemical
series. The order of the more common metals in this series is Zinc,
Iron, Cadmium, Nickel, Lead, Tin, Copper. Each metal is more corrosion
resistant, and said to be "nobler," than the metals which precede it in
the series. If the two metals are iron and copper, the iron will be
corroded since copper is the "nobler" metal. In the case of iron and
zinc, the zinc will be corroded as in this case, iron is the "nobler"
metal. While corrosion is much more severe where dissimilar metals are
involved, electrolytic cells may be formed between areas in the same
metal because of impure or strained areas in the metal itself.

5.03 Corrosion of Brass (De-zincification): Corrosion of the electrochemical
type occurs in certain copper alloys as well as in iron or steel. The
yellow brasses, containing 60 to 67 percent copper and 40 to 33 percent
zinc, are subject to attack by waters in which the pH is below 6.5 or
above 8.5 and the oxygen and carbon dioxide content high. Since copper
is the "nobler" metal, the zinc goes into solution leaving porous,
brittle copper which eventually causes pipe failure. This type of
corrosion which is known as dezincification is more pronounced in hot
water lines as heat accelerates the action.

5.04 The composition of brass piping has an important bearing on its rate of

underwater corrosion. Red brass which contains 85 percent copper and 15 percent zinc is relatively free from corrosion by dezincification.
Copper pipe and tubing

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is even less subject to this type of attack. However, in certain water supply areas where the water is excessively corrosive due to low pH and low carbonate hardness together with a high carbon dioxide content, the corrosive attack on red brass or copper can also be severe.

5.05 Corrosion of Iron and Steel: The composition of iron and steel within the ordinary varieties found commercially has little effect upon the rate of underwater corrosion. Ferrous alloys, such as the so-called stainless steels, are of course much more resistant but due to cost factors they have not been widely used in supply lines and heating plants. Pitting can take place under dirt or rust even in the case of stainless steel.

6.   CORROSION - PREVENTION

6.01 Protective Films: The corrosion of iron and steel may be arrested by the presence of a protective film. Some hard waters naturally produce a protective carbonate film on the metal which arrests corrosion. This, however, is undesirable in heat exchange equipment since it is difficult to control. In tightly closed systems such as a hot water heating system, where there is little make-up water, the elements producing corrosion soon exhaust themselves and corrosion is not apt to be serious.

6.02 Protection by pH Control: Corrosion of ferrous metals may be prevented by raising the alkalinity of water to a pH of 10.0 or higher. This may be accomplished by the use of the common alkalies such as caustic soda, soda ash, trisodium phosphate and sodium silicate. In redwood cooling towers a pH of 8.5 should not be exceeded since the high alkalinity results in de-lignification of the wood fill.

6.03 Protection by Inhibitors: Many chemicals have an inhibiting action on iron and steel, that is, they render the metal passive or inactive toward the corrosion causing elements. These include chromates, bichromates, metalphosphates, nitrates, formaldehyde, amines and soluble oils. These special inhibitors generally do not have boiler water application, their use being confined to engine radiators, air conditioning units, brine systems and other special uses. In using inhibitors it is important that sufficient inhibiting agent be present. If sufficient chemical is present, there is the danger that while some areas will be protected, other areas may be more severely corroded than if no inhibitor were used. Sodium sulphite and hydrazine, although not inhibitors, are also used to prevent corrosion in boilers because they remove oxygen in the water by chemically combining with it. Cyclohexylamine is frequently used in steam heating units. Since it is alkaline and volatile, it establishes a non-corrosive environment in return steam lines.

7.   WATER ANALYSIS

7.01 From discussion thus far it is clear that the properties of water can

only be determined by laboratory tests. There are two distinct types
of water analyses:

the sanitary analysis which indicates the suitability of the water for
human consumption and the mineral analysis, referred to as raw or
make-up water analysis which gives the mineral and gaseous content
affecting its suitability for industrial purposes. The latter type of
analysis, which is the one we are concerned with in this discussion,
usually includes the amount of each of the principal mineral salts
present, the total solids content, and the pH value. For boiler water
use and once through air conditioning systems using well water, the
oxygen and carbon dioxide contents are also important. To be
significant they should be determined at the site. The data, with the
exception of the pH value, are usually expressed in parts per million
although sometimes grains per gallon are used. (1 grain per gallon is
equal to 17.14 parts per million.)

7.02 Methods of Listing Data: In listing the mineral compounds found by a
water analysis, the data may be expressed as so many parts of the
individual bases, plus so many parts of acid radicals. The common
bases are calcium, magnesium, sodium and potassium, while the three
acid radicals most commonly found in water analysis are bicarbonate,
sulphate and chloride. An alternate method is to express the mineral
content as so many parts of each of several compounds such as calcium
bicarbonate, magnesium sulphate, sodium chloride, etc. The first
method is considered better practice as there is no means of
determining with any degree of certainty which bases are associated
with which acid radicals. In either case, since the dissolved gases
are free and uncombined, they are simply shown as parts of oxygen or
carbon dioxide.

7.03 Terms Used in Water Analysis: The individual determinations found in a
water analysis at(d their significance are discussed below:

Total Hardness - Hardness is caused almost entirely by calcium and
magnesium salts. The total hardness as given in water analyses
represents the total of all the calcium and magnesium salts present in
the water calculated to equivalent parts per million of calcium
carbonate. This practice has been adopted for the sake of convenience
and uniformity. It is apparent that although two waters may be
identical in total hardness, the character of scale formed and the
method of treatment may be quite different.

Calcium and Magnesium - Calcium and Magnesium salts constitute 60 to
90 percent of the dissolved mineral matter found in hard water. In
water analyses they are frequently grouped together as total hardness.
In cooling water towers, calcium carbonate is the most readily formed
scale. For this reason, calcium is usually determined separately and
the magnesium hardness taken as the difference.

Silica - This ingredient is generally present in small quantities (10
parts per million or less) but it is particularly troublesome since it
tends to cement the other materials into a very dense tightly adherent
scale.

Iron - While seldom present in natural waters to any appreciable extent, corrosive waters will dissolve iron from the pipes to produce a red rusty water which is objectionable because of its staining action on porcelain fixtures and laundry.

It will also contribute to scale formation, but the quantity present is rarely sufficient to be a source of difficulty from this standpoint.

Sodium and Potassium - In the quantities generally present in public supplies, these salts have little effect on the industrial use of water. However, in treated boiler water they may build up sufficient concentration to cause foaming which may in turn cause priming (carry-over of water with the steam).

Bicarbonate - This is the chief acid radical found in water supplies. Most of the calcium and magnesium present are in the form of bicarbonate. These salts are scale forming since heat decomposes the bicarbonates to form in soluble carbonate which precipitates to form a soft, porous scale. Carbonates as such are present in water supplies to a negligible extent.

Sulphate - Next to bicarbonate, sulphate is the most common acid radical in water. Combined with calcium it forms a dense, hard scale. Sulphates also tend to increase the corrosiveness of water.

Chloride - The quantity of this acid radical found in public supplies varies greatly. Its presence creates a definite tendency toward corrosion. Chloride should not be confused with chlorine which is frequently used to purify public water supplies. The residual quantity of chlorine is normally too small to have any significant effect on the scale forming or corrosive characteristics of water.

Total Solids - This means the total amount of dissolved matter left when the water is evaporated. Since heat is used to evaporate the water, any bicarbonates present are converted to carbonates, water and carbon dioxide. The water and carbon dioxide is evaporated.

Carbon Dioxide and Oxygen - These atmospheric gases, although seldom present to the extent of more than a few parts per million, are the chief causes of corrosion. While oxygen is the actual corrosive agent, the presence of carbon dioxide renders the water acidic and accelerates the rate of corrosion.

pH Value - As discussed in 3.03, the pH scale represents the alkalinity, acidity or neutrality of the water. This is an important part of the analysis since it indicates the greater likelihood of corrosion if the water is acid.

Phenolophthalein and Methyl Orange Alkalinity - Two indicators are commonly used to determine the alkalinity of water - phenolphthalein and methyl orange. The first is pink when the pH is over 8.3, colorless below this point; while methyl orange turns from yellow to red when the pH falls below 4.3. Phenolophthalein alkalinity is uncommon in natural waters but can occur in tower waters as cycles of concentration increase. It is due to the presence of hydrate and carbonate ions and in a cooling tower indicates potential scale

formation. Methyl orange alkalinity is due to the presence of the above and also bicarbonates. It is present at least to some extent in almost all natural waters.

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Other determinations of lesser importance sometimes included in water analyses are nitrates, suspended matter (mud), organic matter (sewage) and oil. These would not normally be found in significant quantities in public water supplies. Oil is sometimes introduced into boilers by heating system return and feed pumps.